Flammability Properties of Polymer Nanocomposites

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• New FR Approach
  – Nanocomposites: particle-filled polymers where at least one dimension of the dispersed particle is nanometer scale.
    • Layered silicate (clay): large aspect ratio - 1D
    • Tube: large aspect ratio - 2D
    • Sphere: aspect ratio of 1 - 3D

  Exceptional physical properties.
• How about their FR performance?
  If effective, what are the effects of the shape of nanoparticles on FR performance?
• If effective, what are their FR mechanisms?
Measurement of Flammability Properties

• **Cone Calorimeter**
  - Oxygen consumption measurement under external thermal radiation (up to 100 kW/m²), ignition delay time, heat release rate, CO, soot, sample mass loss rate, ..

• **Radiative Gasification Device**
  - Mass loss rate measurement in **nitrogen**
Effects of Shape of Nanoparticles

- **Sphere** - Nano silica particles

**Sample Preparation of Silica-PMMA**

1. Mix 14 g of MEK-ST (30% by weight colloidal silica with average 12 nm diameter in MEK, Nissan Chemical) in 40 mL of MMA (Sigma-Aldrich).
2. MEK was removed using a rotary evaporator at 62 °C in low vacuum.
3. Additional MMA was added and mixed in a sonic bath.
4. BPO (1.7% by weight of MMA) was added to make free radical polymerization.
6. The sample was then transferred to a vacuum oven at 80 °C for 72 hours.
7. Control sample was made by substituting MEK-ST with MEK and followed exactly the same procedure.

PMMA(100%)
PMMA(100%)
PMMA(87%) + Nanosilica(13%)
PMMA(87%) + Nanosilica(13%)

Mass Loss Rate (g/m² s)

Time (s)

Picture of the residue of PMMA/Nanosilica
Granular particles
Effects Shape of Nanoparticles

- **Plate** - Clay particles
- **UBE 1015 series of PA6 with 2 % and 5 % MMT.**

Normalized sample weight and weight loss rate curves in N₂ at 10°C/min.
Selected video images at 100s, 200s, and 400s in nitrogen at 50 kW/m².

PA6

PA6/Clay(2%)

PA6/Clay(5%)
Figure 8. HRR plots for the high $M_n$ pure PS, and the high PS/MMT nanocomposites with 2%, 5%, and 10% clay load.
Effects of Shape of Nanoparticles

- Tube – Carbon nanotubes
• **Effects of type of nanotubes?**

Sample behavior during gasification in nitrogen at 50 kW/m²

PMMA/CNT(0.5 %)
In Cone Calorimeter at 50 kW/m²
<table>
<thead>
<tr>
<th>%</th>
<th>SWNT</th>
<th>MWNT</th>
<th>CNF</th>
<th>CB</th>
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Residues collected after nitrogen gasification tests at 50 kW/m²
Effects of dispersion of tubes?

Kashiwagi, et al.
Polymer, 48, 4855, 2007
Fig. 11. The effects of aspect ratio of MWNT on the relationship between mass loss rate peak and mass concentration of MWNT.
• FR Mechanisms

SEM image of the residue of PMMA/SWNT(1%) collected after nitrogen gasification indicating a randomly interlaced structure.

Any relationship between viscoelastic property and FR performance?
Requirements for high FR polymer nanocomposites - to form network structure

- Good dispersion of nanoparticles
- High aspect ratio of nanoparticles
- Need minimum concentration of nanoparticles
- High Mn of resin

- Possible Screening Test
- Viscoelastic measurement to determine the formation of jammed network of initial sample
• Flammability of Polymer nanocomposites:
  • reduce peak heat release rate
  • do not reduce total heat release
  • need further reduction in heat release rate

How ?

1. Nanocomposites plus existing FR additives
2. Enhance char formation (our approach)
   • Combination of clay with catalysts
   • Special functionalization on clay surface
SAN/clay/ZnCl$_2$

- SAN(PS/PAN(75/25))
- Solvent (THF) blending
  - 18 g of SAN in 200 ml of THF
  - 1 g of cloisite 20A and 0.6 g of ZnCl$_2$ in 100 ml of THF
  - Sonication and stirring
  - Drying and annealing
- SAN, SAN/20A(95/5), SAN/ZnCl$_2$(95/3), SAN/20A/ZnCl$_2$(90/5/3), SAN/20A(90/10), SAN/20A/ZnCl$_2$(87/10/3)
SAN/ZnCl₂(97/3)  SAN/20A/ZnCl₂(87/10/3)
Pictures of residues of SAN with additives collected after gasification tests at 50 kW/m² in a nitrogen atmosphere

<table>
<thead>
<tr>
<th>SAN</th>
<th>SAN/ZnCl₂</th>
<th>SAN/20A</th>
<th>SAN/20A/ZnCl₂</th>
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<td>95/5</td>
<td>92/5/3</td>
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Heat Release Rate (kW/m²) vs. Time (s)

- SAN
- SAN/ZnCl₂ (97/3)
- SAN/20A (95/5)
- SAN/20A/ZnCl₂ (92/5/3)
- SAN/20A (90/10)
- SAN/20A/ZnCl₂ (87/10/3)

Heat Release Rate: 50 kW/m²
Clay modification background

Diethylphosphatoethyl triethoxysilane

Potential sites for silane to attach

Clay Structure with hydroxy group on edge or aluminum sites (A sites)
• P containing silane improved the thermal stability of the nanocomposites
Normalized Sample Mass in Cone Calorimeter at 50 kW/m²
Acknowledgement

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